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(54) 【発明の名称】 水素及び一酸化炭素の製造法

(57) 【要約】

【構成】 メタン及び二酸化炭素を含有するガスを触媒に接触させて一酸化炭素と水素を製造する方法において、5配位の Al^{3+} を有するアルミナ含有担体に活性金属を担持した触媒を用いる水素及び一酸化炭素の製造法。

【効果】 本発明によれば、天然ガスの主成分であるメタンと、地球温暖化の主要な原因物質となっている二酸化炭素を用いて、工業的に有用な一酸化炭素と水素を効率良く製造することができる。

【特許請求の範囲】

【請求項 1】 メタン及び二酸化炭素を含有するガスを触媒に接触させて一酸化炭素と水素を製造する方法において、5 配位の Al^{3+} を有するアルミナ含有担体に活性金属を担持した触媒を用いることを特徴とする水素の製造法。

【請求項 2】 メタン及び二酸化炭素を含有するガスを触媒に接触させて一酸化炭素と水素を製造する方法において、5 配位の Al^{3+} を有するアルミナ含有担体に活性金属を担持した触媒を用いることを特徴とする一酸化炭素の製造法。

【請求項 3】 触媒が、5 配位の Al^{3+} を有するアルミナをアルミナ含有担体中に 0.1～50 重量%含有したものである請求項 1 記載の水素の製造法。

【請求項 4】 触媒が、5 配位の Al^{3+} を有するアルミナをアルミナ含有担体中に 0.1～50 重量%含有したものである請求項 2 記載の一酸化炭素の製造法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、天然ガスの主成分であるメタンと、地球温暖化の主要な原因物質となっている二酸化炭素を用いて、工業的に有用な一酸化炭素と水素（以下「合成ガス」と略す）を製造する方法に関する。

【0002】

【従来の技術】 近年、炭酸ガスは地球温暖化の主要原因物質であることから、排出の削減、有効利用が緊急の課題とされている。このため、炭酸ガスの電気的還元法、光合成法、接触水素還元法等の化学的変換方法が検討されている。これらのうち、メタンと二酸化炭素からヒドロホルミル化により、各種有機化合物を合成する際の原料として有用な合成ガスを製造する方法についての報告例は極めて少なく、わずかに、アルミナまたはシリカ担体に 8 族遷移金属担持触媒を使用した接触法 (React. Kinet. catal., 24, 253 (1984) 及び第 68 回触媒討論会 (A) 予稿集, 3H327 (1991)) が知られているにすぎない。

【0003】 しかし、貴金属を担持した触媒は高価であり、経済的に不利である。また貴金属と同等の触媒活性と寿命を有し、より安価な 8 族遷移金属、中でもニッケル触媒は炭素析出傾向が強いため、活性の低下が起こり易いという問題がある。

【0004】

【発明が解決しようとする課題】 従って、本発明は、メタンおよび二酸化炭素を含有するガスから、炭素の析出を抑制し、かつ効率的に一酸化炭素及び水素を製造する方法を提供することを目的とする。

【0005】

【課題を解決するための手段】 このような実情において、本発明者は鋭意検討した結果、メタン及び二酸化炭素を含有するガスを触媒に接触させて一酸化炭素と水素

を製造する方法において、5 配位の Al^{3+} を有するアルミナ含有触媒を用いれば、炭素の析出を抑制し、かつ触媒活性の低下が起こりにくいため、効率良く水素及び一酸化炭素を製造できることを見出し、本発明を完成するに至った。

【0006】 すなわち、本発明は、メタン及び二酸化炭素を含有するガスを触媒に接触させて一酸化炭素と水素を製造する方法において、5 配位の Al^{3+} を有するアルミナを含有担体に活性金属を担持した触媒を用いることを特徴とする水素の製造法を提供するものである。また、本発明は、メタン及び二酸化炭素を含有するガスを触媒に接触させて一酸化炭素と水素を製造する方法において、5 配位の Al^{3+} を有するアルミナ含有担体に活性金属を担持した触媒を用いることを特徴とする一酸化炭素の製造法を提供するものである。

【0007】 本発明で用いられるメタンとしては、メタン単独、メタン含有ガスのいずれでも良い。メタン含有ガスとしては、例えば天然ガス、代替天然ガスが挙げられ、メタンの他に、エタン、プロパン等の飽和炭化水素；エチレン、プロペン、ブテン等の不飽和炭化水素；二酸化炭化水素、微量の硫化水素、10～40 モル%の水素、1～20 モル%の一酸化炭素、窒素、空気または水蒸気を含んでいても良い。

【0008】 本発明において、原料として用いられるメタン及び二酸化炭素のモル比は、メタン／二酸化炭素のモル比が 0.05～25、特に 0.1～20、更に 0.2～10 であるのが好ましい。メタン／二酸化炭素のモル比が 0.05 未満では、リサイクルする二酸化炭素の量が多くなり、水素の収率が減少し、25 を超えると十分な一酸化炭素生成速度が得られなくなり、炭素析出も多く不経済となる。

【0009】 本発明で用いる触媒は、5 配位の Al^{3+} を有するアルミナ含有担体に活性金属を担持したものである。非晶質のアルミナには、4 配位、5 配位、6 配位の 3 種類の Al^{3+} が存在することが知られている (Dupree, Journal De Physique, C8, 113 (1985)) が、本発明で用いるアルミナは、5 配位の Al^{3+} を有するアルミナを含んでいればよく、他に 4 または 6 配位の Al^{3+} を有するアルミナを含んでいてもよい。

【0010】 アルミナ含有担体中、5 配位の Al^{3+} を有するアルミナの配合割合は特に制限されないが、アルミナ含有担体中に 0.1～70 重量%、特に 1～50 重量%であるのが好ましい。0.1 重量%未満では、十分な炭素析出の抑制効果が得られず、70 重量%を超えるものを調整することは難しい。

【0011】 なお、 Al^{3+} の配位状態は、 ^{27}Al -固体 NMR を用いることにより、知ることが出来る。

【0012】 5 配位の Al^{3+} を有するアルミナは、通常の粉碎法、ヒートショック法、有機アルミニウム化合物

のゾルゲル法等により製造することができ、例えば *Journal of Catalysis*, 133, 263 (1992) 及び *Chem. Mater.*, 5, 1204 (1993) に記載されている方法に従って製造することができる。

【0013】すなわち、粉碎法としては、アルミン酸ナトリウム水溶液を一日煮沸し、得られた沈殿物を遠心分離により十分分離し、洗浄した後ジブサイトを得る。次にこのジブサイトを300～600℃で0.1～5時間焼成した後、50～300時間ボールミルで粉碎して5配位の Al^{3+} を有するアルミナを得る方法；ジブサイトと水との混合物を水熱合成してペーマイトを得、次に50～500℃で0.1～100時間ボールミルで粉碎して5配位の Al^{3+} を有するアルミナを得る方法等が挙げられる。

【0014】また、ゾルゲル法としては、アルミニウム-トリセブトキシドのセブチルアルコール溶液と、セブチルアルコールに溶解した尿素溶液との混合溶液に水を添加してゾルを生成させ、熟成後、重炭酸アンモニウムを室温で添加してゲルを沈殿させる。未反応のアルミノブトキシドを除去するため、得られたゲルをセブチルアルコールで十分洗浄し、その後、ゲルを乾燥、焼成し、5配位の Al^{3+} を有するアルミナを得る方法が挙げられる。

【0015】本発明で用いるアルミナ含有担体は、アルミナの他、シリカ、ジルコニア、ニオブ、チタニア、結晶性アルミナシリケート、酸化カルシウム、酸化マグネシウム、酸化バリウム等の金属酸化物を含んでいてもよく、特に酸化カルシウム、酸化マグネシウム、酸化バリウムを含むものは、炭素析出をより有効に抑制することができるため好ましい。これら無機酸化物の配合割合は特に制限されないが、アルミナ含有担体中に0.1～40重量%であるのが好ましい。

【0016】アルミナ含有担体に担持する活性金属としては特に制限されないが、例えばニッケル、ルテニウム、ロジウム、イリジウム、コバルト等の8族遷移金属が好ましく、特にコストの点からニッケルが好ましい。また、これらの金属の酸化物を用いてもよい。

【0017】アルミナ含有担体に担持する活性金属は、全触媒中に、金属換算で0.01～70重量%、特に1.0～50重量%含有されるのが好ましい。0.01重量%未満では十分な二酸化炭素の転化率が得られず、70重量%を超えても、期待するほどの転化率の向上は得られない。

【0018】アルミナ含有担体に活性金属を担持させる方法は特に制限されず、例えば含浸法、ゾルゲル法、物理混合法等公知の方法を用いることが出来る。

【0019】例えば、5配位の Al^{3+} を有するアルミナ成型物をニッケル塩等の金属を含む水溶液に浸漬し、乾燥、焼成後、還元する方法；アルミニウム塩を溶解した

水溶液にアンモニウムを加えて水酸化アルミニウムの沈殿を形成し、得られたゲルを乾燥、焼成した後、ニッケル塩等の金属を含む水溶液に浸漬し、乾燥、焼成後、還元する方法；ニッケル酸化物と5配位の Al^{3+} を有するアルミナとを物理混合し、乾燥、焼成後、還元する方法が挙げられる。

【0020】これらの方法において、触媒を還元する方法としては、還元ガスを用いて行えばよく、触媒を固定化、乾燥後、反応器内で行ってもよい。

【0021】還元ガスとしては純水素、水素・水蒸気、一酸化炭素を用いることができ、水素ガス又は水素・水蒸気ガスが好ましく、特に水素ガスを用いるのが好ましい。また、還元は、メタン及び二酸化炭素を触媒に接触させるときの反応温度で行うことができるが、担持させる活性金属が凝集しないよう200～800℃程度で行うのが好ましい。

【0022】本発明の製造法は、このようにして得られる触媒に、メタン及び二酸化炭素を含有するガスを接触させることにより行われる。このとき反応温度は、300～1000℃、特に400～900℃であるのが好ましい。反応温度が300℃未満ではメタン及び二酸化炭素の十分な転化率が得られず、1000℃を超えると、触媒のシンタリングによる活性の低下が生じる。また、反応圧力は、特に制限されず、常圧～20気圧、特に常圧～10気圧で行うのが好ましい。さらに、原料ガスは、GHSV500～500,000 h^{-1} 、特に1,000～300,000 h^{-1} の速度で供給するのが好ましい。500 h^{-1} 未満では一酸化炭素の生成速度が小さく、また500,000 h^{-1} を超えると原料の転化率が低下し、経済的でない。

【0023】反応方式としては、触媒と原料が効率的に接触できれば特に制限されず、例えば固定床、流動床、移動床で反応を行わせることが出来る。

【0024】

【発明の効果】本発明によれば、メタン及び二酸化炭素を含有するガスを触媒に接触させて一酸化炭素及び水素を製造する方法において、5配位の Al^{3+} を有するアルミナ含有触媒を用いることにより、炭素の析出が抑制され、しかも触媒活性が低下し難いため、メタン及び一酸化炭素の転化率が高く、水素及び一酸化炭素を効率良く得ることができる。

【0025】

【実施例】以下、本発明を実施例によりさらに具体的に説明するが、これは単に例示であって本発明を制限するものではない。

【0026】参考例1

アルミナの調製：1モルのアルミン酸ナトリウム水溶液を1日煮沸して加水分解させ、得られた白色沈殿物を遠心分離し、洗浄してジブサイトを得た。次に、このジブサイトを500℃、1時間焼成し、比較アルミナCを得

た。さらにこのアルミナCを125時間ボールミルで粉碎して5配位 Al^{3+} を有するアルミナAを得た。また、ジブサイト5gと水10mlの混合物をオートクレーブ中、350℃で2日間水熱合成し、ペーマイトを得た。次に、これを400℃で1時間焼成した後、350時間ボールミルで粉碎処理して5配位 Al^{3+} を有するアルミナBを得た。さらに、ペーマイトを600℃で1時間焼成し、比較アルミナDを得た。

【0027】配位数は ^{27}Al -固体NMRにて計測した。 ^{27}Al のケミカルシフトから4配位は65.6ppm、5配位は38.3ppm、6配位は11.4ppmと特定出来、強度比によって、その含有率を試算した。アルミナA～Dの4配位、5配位または6配位を有する Al^{3+} の含有率を表1に、 ^{27}Al -固体NMRスペクトルを図1～4に示した。

【0028】参考例2

触媒Aの調製：アルミナA粉末を打錠成型し、粉碎して20～30メッシュに整粒したアルミナ4.6gを、水9mlに硝酸ニッケル六水和物2.3gを溶解した水溶液に3時間浸漬し、次いで110℃で一晩乾燥した後、500℃で1時間焼成することにより、ニッケル10重量%及びアルミナ90重量%からなる触媒Aを得た。

【0029】参考例3

触媒Bの調製：硝酸ニッケル六水和物の代わりに硝酸ロジウム六水和物を使用した以外は参考例2と同様にし、ロジウム2重量%及びアルミナ98重量%からなる触媒Bを得た。

【0030】参考例4

触媒Cの調製：アルミナB 4.6gを、水9mlに塩化ルテニウム三水和物2.3gを溶解した水溶液に3時間浸漬した後、塩化アンモニウム水溶液で加水分解し、次いで室温で一晩乾燥、さらに110℃で3時間乾燥した後、500℃で1時間焼成することにより、ルテニウム2重量%及びアルミナ98重量%からなる触媒Cを得た。

【0031】参考例5

触媒Dの調製：20～30メッシュに整粒したアルミナB 4.2gを、水8mlに酢酸マグネシウム四水和物2.5gを溶解した水溶液に3時間浸漬した後、110℃で一晩乾燥し、さらに600℃で2時間焼成した。得られた焼成物4.6gを、水5mlに硝酸ニッケル六水和物2.3gを溶解した水溶液に3時間浸漬し、次いで110℃で一晩乾燥した後、500℃で1時間焼成することにより、ニッケル10重量%、酸化マグネシウム27重量%及びアルミナ63重量%からなる触媒Dを得た。

【0032】参考例5

触媒Eの調製：酢酸マグネシウム四水和物の代わりに、酸化カルシウムを使用した以外は参考例5と同様にし、ニッケル10重量%、酸化カルシウム27重量%、及びアルミナ63重量%からなる触媒Eを得た。

【0033】参考例6

触媒Fの調製：20～30メッシュに整粒したアルミナC 14gを、水20mlに硝酸ロジウム六水和物6.9gを溶解した水溶液に3時間浸漬した後、110℃で一晩乾燥し、さらに500℃で1時間焼成することにより、ニッケル10重量%及びアルミナ90重量%からなる触媒Fを得た。

【0034】参考例7

触媒Gの調製：20～30メッシュに整粒したアルミナC 14gを、水20mlに硝酸ニッケル六水和物6.9gを溶解した水溶液に3時間浸漬した後、110℃で一晩乾燥し、さらに500℃で1時間焼成することにより、ロジウム2重量%及びアルミナ98重量%からなる触媒Gを得た。

【0035】参考例8

触媒Hの調製：20～30メッシュに整粒したアルミナD 14gを、水20mlに硝酸ニッケル六水和物6.9gを溶解した水溶液に3時間浸漬した後、110℃で一晩乾燥し、さらに500℃で1時間焼成することにより、ニッケル10重量%及びアルミナ90重量%からなる触媒Fを得た。

【0036】参考例9

触媒Iの調製：アルミナD 14gを、水20mlに硝酸ニッケル六水和物6.9gを溶解した水溶液に3時間浸漬した後、110℃で一晩乾燥し、さらに500℃で1時間焼成することにより、ニッケル10重量%及びアルミナ90重量%からなる触媒Fを得た。

【0037】実施例1～5、比較例1～4

示差熱分析計(DTA-500、セイコー電子工業製)の直径8mm中の α -アルミナ製容器に触媒20mgを充填し、サンプルセル上に装着した後、水素雰囲気下、600℃で1時間還元処理を行い、その後ヘリウム雰囲気下で900℃に昇温した。次に、900℃に保持しながらヘリウムに代えて一酸化炭素(47モル%)、メタン(47モル%)及び窒素(6モル%)の混合ガスを40ml/minで供給し(GHSV150, 0.00hr⁻¹)、水素及び一酸化炭素を得た。反応生成ガスをガスクロマトグラフィー分析し、メタン及び一酸化炭素の転化率および炭素蓄積速度を次式により算出した。結果を表1に示す。

【0038】

【数1】

$$\text{CH}_4\text{転化率}(\%) = \frac{\text{供給CH}_4\text{のモル数} - \text{出口CH}_4\text{のモル数}}{\text{供給CH}_4\text{モル数}} \times 100$$

$$\text{CO}_2\text{転化率}(\%) = \frac{\text{供給CO}_2\text{のモル数} - \text{出口CO}_2\text{のモル数}}{\text{供給CO}_2\text{のモル数}} \times 100$$

$$\text{炭素蓄積速度}(\mu\text{g}/\text{h}\cdot\text{r}^{-1}\cdot\text{g}^{-1}) = \frac{\text{単位時間当たりの蓄積炭素重量}}{\text{触媒重量}}$$

【0039】

【表1】

	触媒	Al ³⁺ 配位数分布 4/5/6 (%/%/%)	CH ₄ 転化率 (%)	CO ₂ 転化率 (%)	収率(%)				炭素蓄積速度 ($\mu\text{g}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$)
					CO	H ₂	C	H ₂ O	
実施例1	A	20/5/75	48	48	49.7	50	0.3	0	0.18
実施例2	B	20/5/75	44	45	49.9	50	0.1	1	0.06
実施例3	C	25/25/50	49	50	49.8	50	0.2	0	0.08
実施例4	D	25/25/50	47	48	49.9	50	0.1	0	0.09
実施例5	E	25/25/50	46	47	49.8	50	0.2	0	0.06
比較例1	F	30/0/70	31	37	43.3	50	6.7	0	4.02
比較例2	G	30/0/70	34	39	49.2	48	0.8	2	0.48
比較例3	H	25/0/75	30	35	46.5	50	4.5	0	2.70
比較例4	J	25/0/75	32	37	49.9	49	0.9	1	0.54

【0040】表1の結果より、5配位Al³⁺を含むアルミナ含有触媒A～Eを用いると、比較触媒F～Iの場合に比べて、メタン及び二酸化炭素の転化率が高く、また触媒上の炭素析出が著しく減少していることがわかる。

【図面の簡単な説明】

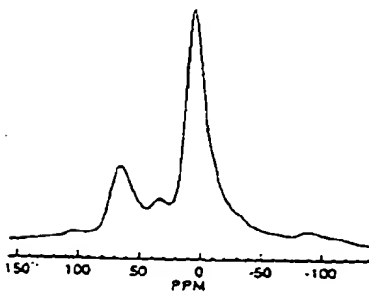
【図1】アルミナAの²⁷Al-固体NMRスペクトルを示す図である。

【図2】アルミナBの²⁷Al-固体NMRスペクトルを示す図である。

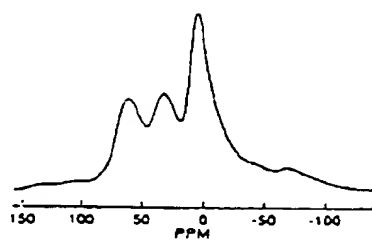
【図3】アルミナCの²⁷Al-固体NMRスペクトルを示す図である。

【図4】アルミナDの²⁷Al-固体NMRスペクトルを示す図である。

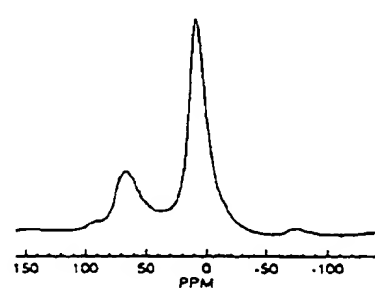
【図1】



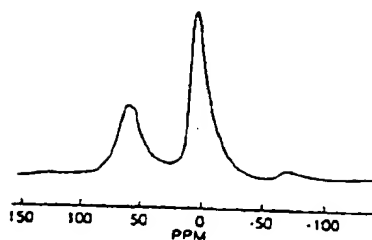
【図2】



【図3】



【図4】



フロントページの続き

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F 1

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PATENT ABSTRACTS OF JAPAN

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(22)Date of filing : 26.12.1994

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(54) PRODUCTION OF HYDROGEN AND CARBON MONOXIDE

(57)Abstract:

PURPOSE: To efficiently produce industrially useful carbon monoxide and hydrogen by using methane which is a main component of natural gas as well as carbon dioxide which is a main substance causing the global warming.

CONSTITUTION: In the production of carbon monoxide and hydrogen by catalyzing methane and carbon dioxide, an activated metal supported on a carrier comprising alumina containing Al^{3+} of coordination number 5 is used as a catalyst.

LEGAL STATUS

[Date of request for examination]

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[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

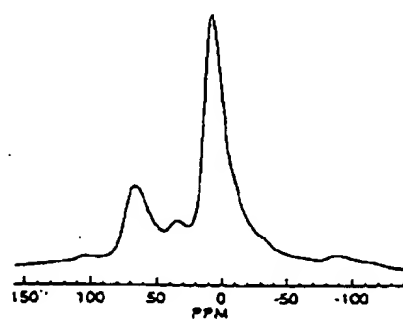
[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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Drawing selection drawing 1

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the method of manufacturing a useful carbon monoxide and useful hydrogen (it abbreviating to "synthesis gas" below) industrially, using the methane which is the principal component of natural gas, and the carbon dioxide used as the main causative agents of global warming.

[0002]

[Description of the Prior Art] In recent years, since carbon dioxide gas is the main causative agent of global warming, let it be the technical problem that curtailment of eccrisis and a deployment are pressing. For this reason, the chemical conversion methods, such as electric reduction of carbon dioxide gas, the photosynthesizing method, and a contact hydrogen reduction method, are considered. There are very few examples of a report about the method of manufacturing synthesis gas useful as a raw material at the time of compounding various organic compounds according to hydroformylation from methane and a carbon dioxide among these, and the contact process (React.Kinet.catal., 24,253 (1984) and the collection of the 68th catalyst (debate A) drafts, 3H327 (1991)) which used 8 group transition-metals support catalyst for an alumina or silica support is known slightly.

[0003] However, the catalyst which supported noble metals is expensive and economically disadvantageous. Moreover, it has catalytic activity and a life equivalent to noble metals, and since the carbon deposit inclination of a nickel catalyst is strong, it has the problem that the fall of activity tends to take place also in cheaper 8 group transition metals.

[0004]

[Problem(s) to be Solved by the Invention] Therefore, from the gas containing methane and a carbon dioxide, this invention suppresses a deposit of carbon and aims at offering the method of manufacturing a carbon monoxide and hydrogen efficiently.

[0005]

[Means for Solving the Problem] In the method of this invention person contacting the gas containing methane and a carbon dioxide for a catalyst in such the actual condition as a result of inquiring wholeheartedly, and manufacturing a carbon monoxide and hydrogen, if the alumina content catalyst which has aluminum³⁺ of 5 coordination is used, since a deposit of carbon is suppressed and the fall of catalytic activity cannot take place easily, it finds out that hydrogen and a carbon monoxide can be manufactured efficiently, and came to complete this invention.

[0006] That is, this invention offers the manufacturing method of the hydrogen characterized by using the catalyst which supported the active metal for the alumina which has aluminum³⁺ of 5 coordination to content support in the method of contacting the gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen. Moreover, this invention offers the manufacturing method of the carbon monoxide characterized by using the catalyst which supported the active metal for the alumina content support which has aluminum³⁺ of 5 coordination in the method of contacting the gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen.

[0007] As methane used by this invention, any of methane independence and methane

content gas are sufficient. As methane content gas, natural gas and substitute natural gas are mentioned, for example, and the unsaturated-hydrocarbon; diacid carbonizing-ized hydrogen, such as saturated-hydrocarbon; ethylene, such as ethane and a propane, a propene, and a butene, the hydrogen sulfide of a minute amount, 10–40–mol % of hydrogen, 1–20–mol % of a carbon monoxide, the nitrogen, the air, or the steam other than methane may be included.

[0008] As for the mole ratio of methane/carbon dioxide, in this invention, it is [the mole ratio of the methane used as a raw material, and a carbon dioxide] desirable 0.05–25, and that it is especially 0.1–20, and also 0.2–10. If the amount of the carbon dioxide which the mole ratio of methane/carbon dioxide recycles less than by 0.05 increases, the yield of hydrogen decreases and 25 is exceeded, sufficient carbon monoxide generation rate will no longer be obtained, and a carbon deposit will also become and uneconomical.

[0009] The catalyst used by this invention supports an active metal to the alumina content support which has aluminum³⁺ of 5 coordination. it is known that 3 kinds of aluminum³⁺ of 4 coordination, 5 coordination, and 6 coordination exists in an amorphous alumina — **** (Dupree, Lournal De Physique, C8,113 (1985)) — the alumina used by this invention may contain the alumina which otherwise has aluminum³⁺ of 4 or 6 coordination that what is necessary is just to include the alumina which has aluminum³⁺ of 5 coordination

[0010] Among alumina content support, especially although especially the blending ratio of coal of an alumina that has aluminum³⁺ of 5 coordination is not restricted, it is desirable in alumina content support that it is 1 – 50 % of the weight 0.1 to 70% of the weight. At less than 0.1 % of the weight, it is difficult to adjust what the depressor effect of sufficient carbon deposit is not obtained, but exceeds 70 % of the weight.

[0011] In addition, the coordination state of aluminum³⁺ can be known by using the ²⁷aluminum–solid–state NMR.

[0012] It can manufacture by the usual grinding method, the HITOSSHOKU method, the sol gel process of an organoaluminium compound, etc., for example, the alumina which has aluminum³⁺ of 5 coordination is Journal. of It can manufacture according to Catalysis, 133,263 (1992) and Chem.Mater., and the method indicated by 5 and 1204 (1993).

[0013] after [namely,] carrying out day boiling of the sodium–aluminate solution, and centrifugal separation's separating enough and washing the obtained settlings as a grinding method — a jib — a site is obtained next, this jib — method; which obtains the alumina which grinds with a ball mill for 50 to 300 hours, and has aluminum³⁺ of 5 coordination after calcinating a site at 300–600 degrees C for 0.1 to 5 hours — a jib — the method of carrying out hydrothermal synthesis of the mixture of a site and water, obtaining a boehmite, and obtaining the alumina which next grinds with a ball mill at 50–500 degrees C for 0.1 to 100 hours, and has aluminum³⁺ of 5 coordination etc. is mentioned

[0014] Moreover, as a sol gel process, add water to the mixed solution of the sec–butyl alcohol solution of aluminum–tree sec butoxide, and the urea solution which dissolved in sec–butyl alcohol, and a sol is made to generate, after digestion, an ammonium bicarbonate is added at a room temperature and gel is settled. In order to remove unreacted aluminobutoxide, the obtained gel is enough washed by sec–butyl alcohol, gel is dried and calcinated after that, and the method of obtaining the alumina which has aluminum³⁺ of 5 coordination is mentioned.

[0015] Since what the alumina content support used by this invention may contain metallic oxides, such as a silica besides an alumina, a zirconia, NIOBIA, a titania, a crystalline alumina silicate, a calcium oxide, a magnesium oxide, and a barium oxide, and contains especially a calcium oxide, a magnesium oxide, and a barium oxide can suppress a carbon deposit more effectively, it is desirable. Although especially the blending ratio of coal of these inorganic oxides is not restricted, it is desirable in alumina content support that it is 0.1 – 40 % of the weight.

[0016] Although not restricted especially as an active metal supported to alumina content support, 8 group transition metals, such as nickel, a ruthenium, a rhodium, iridium, and cobalt, are especially desirable, for example, and nickel is desirable from the point of cost. Moreover, you may use the oxide of these metals.

[0017] As for especially the active metal supported to alumina content support, it is desirable to contain 1.0 to 50% of the weight 0.01 to 70% of the weight by metal conversion in [all] a catalyst. Even if the invert ratio of carbon dioxides enough at less than 0.01 % of the weight is not obtained but it exceeds 70 % of the weight, the improvement in an invert ratio to the extent that it expects is not obtained.

[0018] Especially the method of making alumina content support support an active metal is not restricted, for example, can use well-known methods, such as the sinking-in method, a sol gel process, and physical alligation.

[0019] For example, the alumina molding which has aluminum³⁺ of 5 coordination is immersed in the solution containing metals, such as nickel salt. How to return after dryness and baking: Add ammonium to the solution which dissolved the aluminum salt, and sedimentation of an aluminum hydroxide is formed. The method which is immersed in the solution containing metals, such as nickel salt, and returns after dryness and baking after drying and calcinating the obtained gel; physical mixture of a nickel oxide and the alumina which has aluminum³⁺ of 5 coordination is carried out, and the method of returning is mentioned after dryness and baking.

[0020] In these methods, you may perform a catalyst after fixation and dryness and within a reactor that what is necessary is just to carry out, using a reducing gas as a method of returning a catalyst.

[0021] As a reducing gas, pure hydrogen, hydrogen and a steam, and a carbon monoxide can be used, hydrogen gas, or hydrogen and steam gas is desirable, and it is desirable to use especially hydrogen gas. Moreover, it is desirable to perform reduction at about 200–800 degrees C so that the active metal made to support may not condense, although methane and a carbon dioxide can be performed with the reaction temperature at the time of making a catalyst contact.

[0022] The manufacturing method of this invention is performed by contacting the gas which contains methane and a carbon dioxide for the catalyst acquired by doing in this way. As for especially reaction temperature, at this time, it is desirable that it is 400–900 degrees C 300–1000 degrees C. If sufficient invert ratio of methane and a carbon dioxide is not obtained at less than 300 degrees C but reaction temperature exceeds 1000 degrees C, the fall of the activity by sintering of a catalyst will arise. Moreover, as for especially reaction pressure, it is desirable for it not to be restricted but to carry out with an ordinary pressure – 20 atmospheric pressure, especially an ordinary pressure – 10 atmospheric pressure. Furthermore, it is desirable GHSV500–500,000h⁻¹ and to supply especially material gas at the rate of 1,000–300,000h⁻¹. If the generation rate of a carbon monoxide is small and exceeds 500,000h⁻¹, the invert ratio of a raw material falls and it is not economical at less than [500h –] one.

[0023] As a reaction method, especially if a catalyst and a raw material can contact efficiently, it will not be restricted, for example, it can be made to react by the fixed bed, the fluid bed, and the moving bed.

[0024]

[Effect of the Invention] Since according to this invention a deposit of carbon is suppressed and catalytic activity moreover cannot fall easily by using the alumina content catalyst which has aluminum³⁺ of 5 coordination in the method of contacting the gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen, the invert ratio of methane and a carbon monoxide is high, and hydrogen and a carbon monoxide can be obtained efficiently.

[0025]

[Example] Hereafter, although an example explains this invention still more concretely, this is only instantiation and does not restrict this invention.

[0026] example of reference 1 alumina manufacture: -- the white precipitate which boiled one-mol sodium-aluminate solution on the 1st, was made to understand an added water part, and was obtained -- centrifugal separation -- carrying out -- washing -- a jib -- the site was obtained next, this jib -- 500 degrees C of sites were calcinated for 1 hour, and the

comparison alumina C was obtained. The alumina A which furthermore grinds this alumina C with a ball mill for 125 hours, and has 5 coordination aluminum³⁺ was obtained. moreover, a jib — hydrothermal synthesis of the mixture of 10ml of water was carried out to site 5g for two days at 350 degrees C among the autoclave, and the boehmite was obtained. Next, after calcinating this at 400 degrees C for 1 hour, the alumina B which carries out trituration processing with a ball mill for 350 hours, and has 5 coordination aluminum³⁺ was obtained. Furthermore, the boehmite was calcinated at 600 degrees C for 1 hour, and the comparison alumina D was obtained.

[0027] The coordination number was measured by the ²⁷aluminum–solid–state NMR. For 65.6 ppm and 5 coordination, 38.3 ppm and 6 coordination are [the chemical shift of ²⁷aluminum to 4 coordination] 11.4 ppm. It could specify and the trial calculation of the content was made by the intensity ratio. The content of aluminum³⁺ which has 4 coordination of alumina A–D, 5 coordination, or 6 coordination was shown in Table 1, and the ²⁷aluminum–solid–state NMR spectrum was shown in drawing 1 –4.

[0028] Manufacture of the example [of reference] 2 catalyst A: The catalyst A which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by calcinating alumina 4.6g which carried out tableting molding, ground alumina A powder, and carried out the particle size regulation to 20–30 meshes at 500 degrees C for 1 hour, after being immersed in the solution which dissolved 2.3g of nickel nitrate 6 hydrates in 9ml of water for 3 hours and drying at 110 degrees C subsequently overnight.

[0029] Manufacture of the example [of reference] 3 catalyst B: The catalyst B which consists of 2 % of the weight of rhodiums and 98 % of the weight of aluminas was acquired like the example 2 of reference except having used nitric–acid rhodium 6 hydrate instead of nickel nitrate 6 hydrate.

[0030] Manufacture of the example [of reference] 4 catalyst C: Alumina B After having understood 4.6g an added water part in ammonium–chloride solution after being immersed in the solution which dissolved 2.3g of ruthenium chloride 3 hydrates in 9ml of water for 3 hours, and drying at dryness and 110 more degrees C with a room temperature subsequently for 3 hours overnight, the catalyst C which consists of 2 % of the weight of rutheniums and 98 % of the weight of aluminas was acquired by calcinating at 500 degrees C for 1 hour.

[0031] Manufacture of the example [of reference] 5 catalyst D: Alumina B which carried out the particle size regulation to 20–30 meshes It dried at 110 degrees C overnight, and 4.2g was calcinated at 600 more degrees C for 2 hours, after being immersed in the solution which dissolved 2.5g of magnesium–acetate 4 hydrates in 8ml of water for 3 hours. The catalyst D which consists of 10 % of the weight of nickel, 27 % of the weight of magnesium oxides, and 63 % of the weight of aluminas was acquired by calcinating 4.6g of obtained baking objects at 500 degrees C for 1 hour, after being immersed in the solution which dissolved 2.3g of nickel nitrate 6 hydrates in 5ml of water for 3 hours and drying at 110 degrees C subsequently overnight.

[0032] Manufacture of the example [of reference] 5 catalyst E: Instead of magnesium–acetate 4 hydrate, the catalyst E which consists of 10 % of the weight of nickel, 27 % of the weight of calcium oxides, and 63 % of the weight of aluminas was acquired like the example 5 of reference except having used the calcium oxide.

[0033] Manufacture of the example [of reference] 6 catalyst F: Alumina C which carried out the particle size regulation to 20–30 meshes The catalyst F which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the solution which dissolved 6.9g of nitric–acid rhodium 6 hydrates in 20ml of water for 3 hours.

[0034] Manufacture of the example [of reference] 7 catalyst G: Alumina C which carried out the particle size regulation to 20–30 meshes The catalyst G which consists of 2 % of the weight of rhodiums and 98 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the solution which dissolved 6.9g of nickel nitrate 6 hydrates in 20ml of water for 3 hours.

[0035] Manufacture of the example [of reference] 8 catalyst H: Alumina D which carried out

the particle size regulation to 20-30 meshes The catalyst F which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the solution which dissolved 6.9g of nickel nitrate 6 hydrates in 20ml of water for 3 hours.

[0036] Manufacture of the example [of reference] 9 catalyst I: Alumina D The catalyst F which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the solution which dissolved 6.9g of nickel nitrate 6 hydrates in 20ml of water for 3 hours.

[0037] After filling up the container made from an alpha alumina in the diameter of 8mm of one to examples 1-5 and example of comparison 4 differential thermal analyzer (DTA-500, product made from the SEIKO electronic industry) with 20mg of catalysts and equipping on a sample cell, reduction processing was performed at 600 degrees C under hydrogen atmosphere for 1 hour, and the temperature up was carried out to 900 degrees C under helium atmosphere after that. Next, it replaced with helium, the mixed gas of a carbon dioxide (47-mol %), methane (47-mol %), and nitrogen (six-mol %) was supplied by 40 ml/min, holding at 900 degrees C, (GHSV150,000hr⁻¹), and hydrogen and the carbon monoxide were obtained. Gas-chromatography analysis of the reaction generation gas was carried out, and the invert ratio and carbon accumulation speed of methane and a carbon dioxide were computed by the following formula. A result is shown in Table 1.

[0038]

[Equation 1]

$$\text{CH}_4\text{転化率 (\%)} = \frac{\text{供給CH}_4\text{のモル数} - \text{出口CH}_4\text{のモル数}}{\text{供給CH}_4\text{モル数}} \times 100$$

$$\text{CO}_2\text{転化率 (\%)} = \frac{\text{供給CO}_2\text{のモル数} - \text{出口CO}_2\text{のモル数}}{\text{供給CO}_2\text{のモル数}} \times 100$$

$$\text{炭素蓄積速度 (\mu g / h r^{-1} \cdot g^{-1})} = \frac{\text{単位時間当たりの蓄積炭素重量}}{\text{触媒重量}}$$

[0039]

[Table 1]

	触媒	Al ³⁺ 配位数分布 4 / 5 / 6 (% / % / %)	CH ₄ 転化率 (%)	CO ₂ 転化率 (%)	収率 (%)				炭素蓄積速度 ($\mu\text{g} \cdot \text{h r}^{-1} \cdot \text{g}^{-1}$)
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比較例 4	J	25/0/75	32	37	49.9	49	0.9	1	0.54

[0040] When alumina content catalyst A-E containing 5 coordination aluminum³⁺ is used, compared with the case of comparison catalyst F-I, the invert ratio of methane and a carbon

dioxide is high, and the result of Table 1 shows that the carbon deposit on a catalyst is decreasing remarkably.

[Translation done.]

JAPANESE [JP,08-175805,A] *Cited Reference*

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS
DRAWINGS

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CLAIMS

[Claim(s)]

[Claim 1] A manufacturing method of hydrogen characterized by using a catalyst which supported an active metal to alumina content support which has aluminum³⁺ of 5 coordination in a method of contacting gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen.

[Claim 2] A manufacturing method of a carbon monoxide characterized by using a catalyst which supported an active metal to alumina content support which has aluminum³⁺ of 5 coordination in a method of contacting gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen.

[Claim 3] A manufacturing method of hydrogen according to claim 1 to which a catalyst contains an alumina which has aluminum³⁺ of 5 coordination 0.1 to 50% of the weight in alumina content support.

[Claim 4] A manufacturing method of a carbon monoxide according to claim 2 with which a catalyst contains an alumina which has aluminum³⁺ of 5 coordination 0.1 to 50% of the weight in alumina content support.

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[0002]

[Description of the Prior Art] In recent years, since carbon dioxide gas is the main causative agent of global warming, let it be the technical problem that the cutback of blowdowns and a deployment are pressing. For this reason, the chemical conversion methods, such as electric reduction of carbon dioxide gas, the photosynthesizing method, and a contact hydrogen reduction method, are considered. There are very few examples of a report about the method of manufacturing synthesis gas useful as a raw material at the time of compounding various organic compounds by the hydroformylation from methane and a carbon dioxide among these, and the contact process (React.Kinet.catal., 24,253 (1984) and the collection of the 68th catalyst (debate A) drafts, 3H327 (1991)) which used 8 group transition-metals support catalyst for an alumina or silica support is known slightly.

[0003] However, the catalyst which supported noble metals is expensive and economically disadvantageous. Moreover, it has catalytic activity and a life equivalent to noble metals, and since the carbon deposit inclination of a nickel catalyst is strong, it has the problem that lowering of activity tends to take place also in cheaper 8 group transition metals.

[0004]

[Problem(s) to be Solved by the Invention] Therefore, from the gas containing methane and a carbon dioxide, this invention controls a deposit of carbon and aims at offering the method of manufacturing a carbon monoxide and hydrogen efficiently.

[0005]

[Means for Solving the Problem] In a method of this invention person contacting gas containing methane and a carbon dioxide for a catalyst in such the actual condition as a result of inquiring wholeheartedly, and manufacturing a carbon monoxide and hydrogen, if an alumina content catalyst which has aluminum³⁺ of 5 coordination is used, since a deposit of carbon is controlled and lowering of catalytic activity cannot take place easily, it came to complete a header and this invention for the ability of hydrogen and a carbon monoxide to be manufactured efficiently.

[0006] That is, this invention offers a manufacturing method of hydrogen characterized by using a catalyst which supported an active metal for an alumina which has aluminum³⁺ of 5 coordination to content support in a method of contacting gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen. Moreover, this invention offers a manufacturing method of a carbon monoxide characterized by using a catalyst which supported an active metal for alumina content support which has aluminum³⁺ of 5 coordination in a method of contacting gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen.

[0007] As methane used by this invention, any of methane independence and methane content gas are sufficient. As methane content gas, natural gas and substitute natural gas are

mentioned, for example, and unsaturated hydrocarbon; diacid carbonizing-ized hydrogen, such as saturated hydrocarbon; ethylene, such as ethane and a propane, a propene, and a butene, a hydrogen sulfide of a minute amount, 10–40-mol % of hydrogen, 1–20-mol % of a carbon monoxide, nitrogen, air, or a steam other than methane may be included.

[0008] In this invention, 0.05–25, and that it is especially 0.1–20, and also 0.2–10 have [a mole ratio of methane used as a raw material, and a carbon dioxide] a desirable mole ratio of methane/carbon dioxide. If an amount of a carbon dioxide which a mole ratio of methane/carbon dioxide recycles less than by 0.05 increases, yield of hydrogen decreases and 25 is exceeded, sufficient carbon monoxide generation rate will no longer be obtained, and a carbon deposit will also become and uneconomical.

[0009] A catalyst used by this invention supports an active metal to alumina content support which has aluminum³⁺ of 5 coordination. it is known that 3 kinds of aluminum³⁺ of 4 coordination, 5 coordination, and 6 coordination exists in an amorphous alumina -- **** (Dupree, Lournal De Physique, C8,113 (1985)) -- an alumina used by this invention may contain an alumina which otherwise has aluminum³⁺ of 4 or 6 coordination that what is necessary is just to include an alumina which has aluminum³⁺ of 5 coordination.

[0010] Among alumina content support, especially although especially the blending ratio of coal of an alumina that has aluminum³⁺ of 5 coordination is not restricted, it is desirable in alumina content support that it is 1 – 50 % of the weight 0.1 to 70% of the weight. At less than 0.1 % of the weight, it is difficult to adjust what depressor effect of sufficient carbon deposit is not acquired, but exceeds 70 % of the weight.

[0011] In addition, a coordination condition of aluminum³⁺ can be known by using the ²⁷aluminum–solid–state NMR.

[0012] an alumina which has aluminum³⁺ of 5 coordination -- the usual grinding method and HITOSSHOKU -- law, a sol gel process of an organoaluminium compound, etc. -- it can manufacture -- for example, Journal of It can manufacture according to Catalysis, 133,263 (1992) and Chem.Mater., and a method indicated by 5 and 1204 (1993).

[0013] after [namely,] carrying out day boiling of the sodium–aluminate aqueous solution, and centrifugal separation's separating enough and washing obtained settlings as a grinding method -- a jib -- a site is obtained. next, this jib -- method; which obtains an alumina which grinds with a ball mill for 50 to 300 hours, and has aluminum³⁺ of 5 coordination after calcinating a site at 300–600 degrees C for 0.1 to 5 hours -- a jib -- a method of carrying out hydrothermal synthesis of the mixture of a site and water, obtaining boehmite, and obtaining an alumina which grinds with a ball mill at 50–500 degrees C next for 0.1 to 100 hours, and has aluminum³⁺ of 5 coordination etc. is mentioned.

[0014] Moreover, as a sol gel process, add water to a mixed solution of a sec-butyl alcohol solution of aluminum–tree sec butoxide, and a urea solution which dissolved in sec-butyl alcohol, and a sol is made to generate, after aging, ammonium bicarbonate is added at a room temperature and gel is settled. In order to remove unreacted alumino butoxide, sec-butyl alcohol washes obtained gel enough, gel is dried and calcinated after that, and a method of obtaining an alumina which has aluminum³⁺ of 5 coordination is mentioned.

[0015] Since what alumina content support used by this invention may contain metallic oxides, such as a silica besides an alumina, a zirconia, NIOBIA, a titania, crystalline alumina silicate, a calcium oxide, a magnesium oxide, and a barium oxide, and contains especially a calcium oxide, a magnesium oxide, and a barium oxide can control a carbon deposit to validity more, it is desirable. Although especially the blending ratio of coal of these inorganic oxides is not restricted, it is desirable in alumina content support that it is 0.1 – 40 % of the weight.

[0016] Although not restricted especially as an active metal supported to alumina content support, 8 group transition metals, such as nickel, a ruthenium, a rhodium, iridium, and cobalt, are especially desirable, for example, and nickel is desirable from a point of cost. Moreover, an oxide of these metals may be used.

[0017] As for especially an active metal supported to alumina content support, it is desirable to contain 1.0 to 50% of the weight 0.01 to 70% of the weight by metal conversion in [all] a catalyst. Even if an invert ratio of carbon dioxides enough at less than 0.01 % of the weight is

not obtained but it exceeds 70 % of the weight, improvement in an invert ratio to the extent that it expects is not obtained.

[0018] Especially a method of making alumina content support support an active metal is not restricted, for example, can use well-known methods, such as an impregnation method, a sol gel process, and physical alligation.

[0019] For example, alumina molding which has aluminum³⁺ of 5 coordination is immersed in an aqueous solution containing metals, such as nickel salt. How to return after desiccation and baking; Add ammonium to an aqueous solution which dissolved an aluminum salt, and precipitation of an aluminum hydroxide is formed. A method which is immersed in an aqueous solution containing metals, such as nickel salt, and returns after desiccation and baking after drying and calcinating obtained gel; physical mixing of a nickel oxide and the alumina which has aluminum³⁺ of 5 coordination is carried out, and a method of returning is mentioned after desiccation and baking.

[0020] In these methods, a catalyst may be performed after immobilization and desiccation and within a reactor that what is necessary is just to carry out, using reducing gas as a method of returning a catalyst.

[0021] As reducing gas, pure hydrogen, hydrogen and a steam, and a carbon monoxide can be used, hydrogen gas, or hydrogen and steam gas is desirable, and it is desirable to use especially hydrogen gas. Moreover, although reduction can perform methane and a carbon dioxide with reaction temperature at a time of making a catalyst contact, it is desirable to carry out at about 200–800 degrees C so that an active metal made to support may not condense.

[0022] A manufacturing method of this invention is performed by contacting gas which contains methane and a carbon dioxide for a catalyst acquired by doing in this way. As for especially reaction temperature, at this time, it is desirable that it is 400–900 degrees C 300–1000 degrees C. If sufficient invert ratio of methane and a carbon dioxide is not obtained at less than 300 degrees C but reaction temperature exceeds 1000 degrees C, lowering of activity by sintering of a catalyst will arise. Moreover, as for especially reaction pressure, it is desirable for it not to be restricted but to carry out with ordinary pressure – 20 atmospheric pressure, especially ordinary pressure – 10 atmospheric pressure. Furthermore, it is desirable GHSV500–500,000h⁻¹ and to supply especially material gas at the rate of 1,000–300,000h⁻¹. If a generation rate of a carbon monoxide is small and exceeds 500,000h⁻¹, an invert ratio of a raw material falls and it is not economical at less than [500h –] one.

[0023] As a reaction method, especially if a catalyst and a raw material can contact efficiently, it will not be restricted, for example, it can be made to react in the fixed bed, the fluid bed, and the moving bed.

[0024]

[Effect of the Invention] Since according to this invention a deposit of carbon is controlled and catalytic activity moreover cannot fall easily by using the alumina content catalyst which has aluminum³⁺ of 5 coordination in the method of contacting the gas containing methane and a carbon dioxide for a catalyst, and manufacturing a carbon monoxide and hydrogen, the invert ratio of methane and a carbon monoxide is high, and hydrogen and a carbon monoxide can be obtained efficiently.

[0025]

[Example] Hereafter, although an example explains this invention still more concretely, this is only instantiation and does not restrict this invention.

[0026] example of reference 1 alumina preparation: -- the white sediment which will boil an one-mol sodium-aluminate aqueous solution for one day, was made to hydrolyze, and was obtained -- centrifugal separation -- carrying out -- washing -- a jib -- the site was obtained. next, this jib -- 500 degrees C of sites were calcinated for 1 hour, and the comparison alumina C was obtained. The alumina A which furthermore grinds this alumina C with a ball mill for 125 hours, and has 5 coordination aluminum³⁺ was obtained. moreover, a jib -- hydrothermal synthesis of the mixture of 10ml of water was carried out to site 5g for two days at 350 degrees C among the autoclave, and boehmite was obtained. Next, after

calcinating this at 400 degrees C for 1 hour, the alumina B which carries out grinding processing with a ball mill for 350 hours, and has 5 coordination aluminum³⁺ was obtained. Furthermore, boehmite was calcinated at 600 degrees C for 1 hour, and the comparison alumina D was obtained.

[0027] The coordination number was measured by the ²⁷aluminum-solid-state NMR. For 65.6 ppm and 5 coordination, 38.3 ppm and 6 coordination are [the chemical shift of ²⁷aluminum to 4 coordination] 11.4 ppm. It could specify and the trial calculation of the content was made by the intensity ratio. The content of aluminum³⁺ which has 4 coordination of alumina A-D, 5 coordination, or 6 coordination was shown in a table 1, and the ²⁷aluminum-solid-state NMR spectrum was shown in drawing 1 -4.

[0028] Preparation of the example [of reference] 2 catalyst A: The catalyst A which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by calcinating alumina 4.6g which carried out making tablet molding, ground alumina A powder, and carried out the particle size regulation to 20-30 meshes at 500 degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 2.3g of nickel nitrate 6 hydrates in 9ml of water for 3 hours and drying at 110 degrees C subsequently overnight.

[0029] Preparation of the example [of reference] 3 catalyst B: The catalyst B which consists of 2 % of the weight of rhodiums and 98 % of the weight of aluminas was acquired like the example 2 of reference except having used nitric-acid rhodium 6 hydrate instead of nickel nitrate 6 hydrate.

[0030] Preparation of the example [of reference] 4 catalyst C: Alumina B After having hydrolyzed 4.6g in the ammonium-chloride aqueous solution after being immersed in the aqueous solution which dissolved 2.3g of ruthenium chloride 3 hydrates in 9ml of water for 3 hours, and drying at desiccation and 110 more degrees C with a room temperature subsequently for 3 hours overnight, the catalyst C which consists of 2 % of the weight of rutheniums and 98 % of the weight of aluminas was acquired by calcinating at 500 degrees C for 1 hour.

[0031] Preparation of the example [of reference] 5 catalyst D: Alumina B which carried out the particle size regulation to 20-30 meshes It dried at 110 degrees C overnight, and 4.2g was calcinated at 600 more degrees C for 2 hours, after being immersed in the aqueous solution which dissolved 2.5g of magnesium acetate 4 hydrates in 8ml of water for 3 hours. The catalyst D which consists of 10 % of the weight of nickel, 27 % of the weight of magnesium oxides, and 63 % of the weight of aluminas was acquired by calcinating 4.6g of obtained baking objects at 500 degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 2.3g of nickel nitrate 6 hydrates in 5ml of water for 3 hours and drying at 110 degrees C subsequently overnight.

[0032] Preparation of the example [of reference] 5 catalyst E: Instead of magnesium acetate 4 hydrate, the catalyst E which consists of 10 % of the weight of nickel, 27 % of the weight of calcium oxides, and 63 % of the weight of aluminas was acquired like the example 5 of reference except having used the calcium oxide.

[0033] Preparation of the example [of reference] 6 catalyst F: Alumina C which carried out the particle size regulation to 20-30 meshes The catalyst F which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 6.9g of nitric-acid rhodium 6 hydrates in 20ml of water for 3 hours.

[0034] Preparation of the example [of reference] 7 catalyst G: Alumina C which carried out the particle size regulation to 20-30 meshes The catalyst G which consists of 2 % of the weight of rhodiums and 98 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 6.9g of nickel nitrate 6 hydrates in 20ml of water for 3 hours.

[0035] Preparation of the example [of reference] 8 catalyst H: Alumina D which carried out the particle size regulation to 20-30 meshes The catalyst F which consists of 10 % of the

weight of nickel and 90 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 6.9g of nickel nitrate 6 hydrates in 20ml of water for 3 hours.

[0036] Preparation of the example [of reference] 9 catalyst I: Alumina D The catalyst F which consists of 10 % of the weight of nickel and 90 % of the weight of aluminas was acquired by drying at 110 degrees C overnight and calcinating 14g at 500 more degrees C for 1 hour, after being immersed in the aqueous solution which dissolved 6.9g of nickel nitrate 6 hydrates in 20ml of water for 3 hours.

[0037] After filling up the container made from alpha-alumina in the diameter of 8mm of one to examples 1-5 and example of comparison 4 differential thermal analyzer (DTA-500, product made from the SEIKO electronic industry) with 20mg of catalysts and equipping on a sample cel, reduction processing was performed at 600 degrees C under the hydrogen ambient atmosphere for 1 hour, and temperature up was carried out to 900 degrees C under the helium ambient atmosphere after that. Next, it replaced with helium, the mixed gas of a carbon dioxide (47-mol %), methane (47-mol %), and nitrogen (six-mol %) was supplied by 40 ml/min, holding at 900 degrees C, (GHSV150,000hr⁻¹), and hydrogen and a carbon monoxide were obtained. Gas-chromatography analysis of the reaction generation gas was carried out, and the invert ratio and carbon are recording speed of methane and a carbon dioxide were computed by the degree type. A result is shown in a table 1.

[0038]

[Equation 1]

$$\text{CH}_4\text{転化率 (\%)} = \frac{\text{供給CH}_4\text{のモル数} - \text{出口CH}_4\text{のモル数}}{\text{供給CH}_4\text{モル数}} \times 100$$

$$\text{CO}_2\text{転化率 (\%)} = \frac{\text{供給CO}_2\text{のモル数} - \text{出口CO}_2\text{のモル数}}{\text{供給CO}_2\text{のモル数}} \times 100$$

$$\text{炭素蓄積速度 (\mu g / h r^{-1} \cdot g^{-1})} = \frac{\text{単位時間当たりの蓄積炭素重量}}{\text{触媒重量}}$$

[0039]

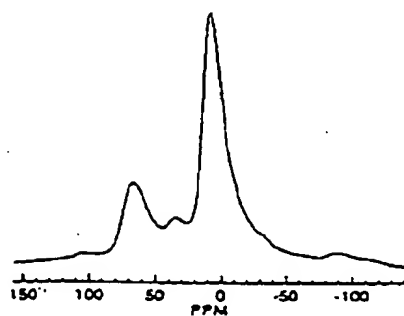
[A table 1]

	触媒	Al ³⁺ 配位数分布 4 / 5 / 6 (% / % / %)	CH ₄ 転化率 (%)	CO ₂ 転化率 (%)	収率 (%)				炭素蓄積速度 (μg · hr ⁻¹ · g ⁻¹)
					CO	H ₂	C	H ₂ O	
実施例 1	A	20/5/75	48	48	49.7	50	0.3	0	0.18
実施例 2	B	20/5/75	44	45	49.9	50	0.1	1	0.06
実施例 3	C	25/25/50	49	50	49.8	50	0.2	0	0.08
実施例 4	D	25/25/50	47	48	49.9	50	0.1	0	0.09
実施例 5	E	25/25/50	46	47	49.8	50	0.2	0	0.06
比較例 1	F	30/0/70	31	37	43.3	50	6.7	0	4.02
比較例 2	G	30/0/70	34	39	49.2	48	0.8	2	0.48
比較例 3	H	25/0/75	30	35	46.5	50	4.5	0	2.70
比較例 4	J	25/0/75	32	37	49.9	49	0.9	1	0.54

[0040] When alumina content catalyst A-E containing 5 coordination aluminum³⁺ is used, compared with the case of comparison catalyst F-I, the invert ratio of methane and a carbon

dioxide is high, and the result of a table 1 shows that the carbon deposit on a catalyst is decreasing remarkably.

[Translation done.]

Drawing selection drawing 1

[Translation done.]